

Formation, Occurrence and Analysis of Polychlorinated Dibenzofurans, Dioxins and Related Compounds

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In several accidents (fires, explosions) involving electrical systems containing polychlorinated biphenyls (PCBs) or benzenes (PCBZs), the formation of polychlorinated tricyclic aromatic compounds such as polychlorinated dibenzofurans (PCDFs), dibenzo-*p*-dioxins (PCDDs) and biphenylenes (PCBPs) was observed. These findings were not surprising in light of our previous studies on the formation of PCDFs and PCDDs from the thermolysis (500–750°C in presence of air) of PCBs or PCBZs. In these experiments we identified three main and a fourth minor reaction pathway leading to PCDFs from PCBs. The three main reactions involved the loss of *ortho*-Cl₂, and the losses of *ortho*-HCl with and without a 2,3-chlorine shift. The fourth, minor reaction route found with some PCBs, involved the loss of *ortho*-H₂. These reaction pathways were intramolecular cyclizations via oxidation to phenolic compounds. Thermolysis of commercial PCBs (Aroclor 1254 and 1260) yielded the same PCDF isomers as expected from the main PCB components via these four reaction pathways; the isomers formed included the toxic 2,3,7,8-substituted tetra-, penta- and hexa-CDFs. Thermolysis of PCBZs involved complex condensation reactions with multiple rearrangements leading to PCDFs as well as PCDDs. Again oxidation to phenolic products was involved but the reaction routes are not yet fully elucidated.

The results of samples from transformer and capacitor accident sites showed very complex PCDF mixtures with 2,3,7,8-substituted isomers as main components and originating from the PCBs in the transformer liquid. The unusual presence of PCDDs in samples from the Binghamton accident originates from PCBZs present in transformer fluid of that specific installation, thus confirming our previous thermolysis findings. The source of PCBPs and their route of formation have not yet been fully elucidated. The application of high-resolution gas chromatography in combination with mass spectrometry is documented and the need for isomer-specific analyses discussed.

Introduction

Polychlorinated tricyclic aromatic compounds have been identified in several accidents involving transformers and capacitors with polychlorinated biphenyls (PCBs) and benzenes (PCBZs) (1,2). This group of compounds includes some of the most toxic synthetic chemicals known. The formations and possible release of these compounds in accidents from electrical system failures (fires, explosions, overheating) with involvement of PCBs and PCBZs constitutes a new, previously unrecognized health hazard and environmental contaminations as well as occupational exposures with these chemicals have to be prevented.

The group of tricyclic aromatic compounds of concern here is consisting of three series, namely the polychlorinated dibenzofurans (PCDFs), dibenzo-*p*-dioxins (PCDDs) and biphenylenes (PCBPs). Substitution by chlorine of these ring systems leads to a number of

chloro homologs and isomers ranging from the mono- to the fully chlorinated octachloro compounds. There is a total of 135 PCDF, 75 PCDD and 75 PCBP isomers (see Table 1). The largest number of isomers in all three series is found for the tetrachloro compounds, namely 38 tetrachlorodibenzofurans (tetra-CDFs), 22 tetrachlorodibenzo-*p*-dioxins (tetra-CDDs) and 22 tetrachlo-

Table 1. Possible number of positional PCDF, PCDD and PCBP isomers.

Chlorine substitution	Number of isomers		
	PCDFs	PCDDs	PCBPs
Mono-	4	2	2
Di-	16	10	10
Tri-	28	14	14
Tetra-	38	22	22
Penta-	28	14	14
Hexa-	16	10	10
Hepta-	4	2	2
Octa-	1	1	1
Total	135	75	75

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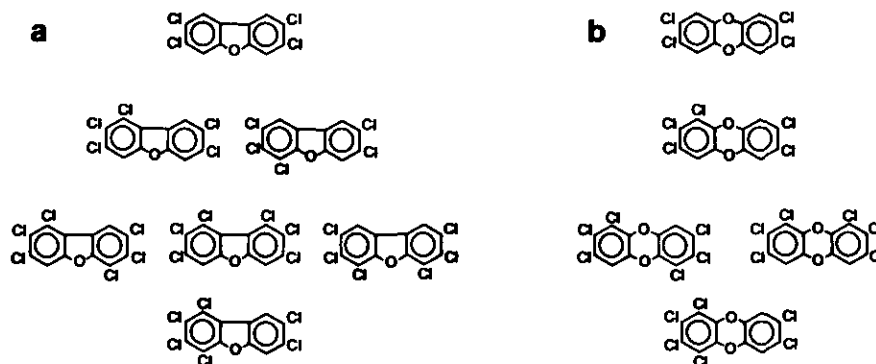


FIGURE 1. Structures of toxic and hazardous 2,3,7,8-substituted tetra-, penta- and hexachlorodibenzofurans and -dibenzo-*p*-dioxins (a)/(b).

robiphenylenes (tetra-CBPs). The large number of isomers is one of the reasons for the complexity and difficulty of the analyses.

Some of these compounds proved extremely toxic and hazardous (3-7). LD₅₀-values range from 1 to 100 µg/kg for the most sensitive laboratory animal species. There is a great deal of toxicity data on PCDDs, especially on 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-tetra-CDD), and some on PCDFs, but comparatively little on PCBPs. However, from structural considerations and from the biological activity of some congeners, the PCDFs and PCBPs have to be considered as in similar toxicity as the PCDDs (6,7).

Toxicity seems to depend on the number and the position of the chlorine substituents of a congener (4,5). It is highest for the tetra-, penta- and hexachloro compounds. Pronounced differences in toxicity are found between isomers. Toxicity apparently is highest for isomers fully chlorinated at the lateral (2-, 3-, 7- and 8- in PCDFs and PCDDs, 2-, 3-, 6- and 7-in PCBPs) positions (5,7). The most hazardous compounds are thus the so-called 2,3,7,8 (2,3,6,7)-substituted isomers. There are seven such isomers in the PCDF series, and five each in the series of the PCDDs and PCBPs. The structures of the 2,3,7,8-substituted PCDFs and PCDDs are shown in Figure 1a and 1b, respectively. The most toxic isomer appears to be 2,3,7,8-tetra-CDD that also has a high cocarcinogenic potential (8). The most toxic members of the other two series are expected to be 2,3,7,8-tetra-CDF and 2,3,6,7-tetra-CBP; both compounds are isosteric to 2,3,7,8-tetra-CDD. PCDDs and PCDFs have caused environmental contaminations (Seveso, Vietnam, Love Canal, Missouri) and human intoxications (Yusho in Japan and Taiwan); they have received wide public attention. Comparatively little is known about the PCBPs.

PCDDs and PCDFs are found as undesired trace contaminants in certain industrial chemicals such as the chlorophenols and their derivatives (2,3,7,8-tetra-CDD is a contaminant of 2,4,5-trichlorophenol and 2,4,5-T herbicides) and PCBs (9). The levels of PCDDs and PCDFs are usually in the ppm or sub-ppm range, nevertheless the presence of these contaminants proved to be responsible for some of the toxic properties of these

Table 2. Levels of PCDFs in commercial PCBs.

Sample	PCDF level, ppm					Total
	Tri-	Tetra-	Penta-	Hexa-	Hepta-	
Aroclor 1254	0.10	0.25	0.70	0.81	—	1.9
Aroclor 1254 (lot KK602)	—	0.05	0.10	0.02	—	0.2
Aroclor 1260	0.06	0.30	1.00	1.10	1.35	3.8
Clorphen T64	0.10	0.30	1.73	2.45	0.82	5.4
Prodelec 3010	0.41	1.08	0.35	0.07	—	2.0
Mitsubishi (used)	2.13	4.00	3.30	0.53	—	10.0

industrial chemicals. Of special interest here is the presence of PCDFs in PCBs. These industrial chemicals were used in very large quantities (world production above 1 million tons) in many applications. Due to their good electrical properties, their nonflammability and chemical stability they were used in electrical systems as transformer and capacitor fluids. Among the many commercial products were Aroclors, Clophenes, Phenoclor, Phenalenes, Pyranols, Kanechlor and many others. Aroclor 1254 and 1260 were preferred products in the U.S.; they had an average composition containing 54 and 60% chlorine, respectively. The unrestricted industrial use of PCBs caused a large scale environmental contamination. At least one manufacturer restricted production and sales of PCBs in the 1970s to closed systems (capacitors and transformers). Chlorobenzenes apparently were added sometimes to these products in specific applications (2).

Commercial PCBs were shown to contain PCDFs as impurities (9,10). The toxicity of some PCB formulations was responsible for the search and the finding of PCDFs as toxic agents (10). The levels of PCDFs in some commercial PCBs surveyed are listed in Table 2; other tricyclic compounds (PCDDs and PCBPs) were not present in these samples (Buser and Rappe, unpublished, 1979). The samples analyzed showed rather complex isomeric mixtures of PCDFs. Among the isomers identified were 2,3,7,8-substituted congeners such as 2,3,7,8-tetra-, 1,2,3,7,8- and 2,3,4,7,8-penta-, and 1,2,3,4,7,8-hexa-CDF. Additional isomers found were 2,3,6,8- and 2,3,6,7-tetra-, 1,2,4,7,8-penta-, 1,2,4,6,7,8- and 1,2,4,6,8,9-hexa-, and 1,2,3,4,6,7,8- and 1,2,3,4,6,8,9-hepta-CDF. A sample of used PCB showed increased

levels of PCDFs (Table 2). Significantly increased levels of PCDFs were calculated for the PCB causing the Yu-sho poisoning in Japan (11). In that incident, PCB used as a heat transfer liquid was oxidized and contaminated rice oil for human consumption via a faulty heating system.

PCDFs and PCDDs are known to be formed in thermal reactions from suitable precursors such as from chlorophenols, PCBs and PCBZs (12-14). They have also been detected in emissions and fly ash from municipal and industrial incinerators (15,16). PCDDs and PCDFs are also suspected to be formed, although in extremely low yields, from more common substances like lignin by chlorination reactions under incineration conditions (17). Of special interest here is their formation by thermal reactions from PCBs and PCBZs.

Formation of PCDFs from the Thermolysis of PCBs

In 1978, we reported the conversion of PCBs into PCDFs via thermolytic reactions in laboratory experiments (13). Although this reaction was anticipated, surprisingly, no experimental evidence had been previously reported. Up to that time little attention was actually paid to the possible formation of PCDFs from incineration or combustion of PCBs.

In our laboratory experiments, we demonstrated the conversion to PCDFs from small quantities (100 μ g) of commercial PCBs (Aroclor 1254 and 1260) at temperatures from 500 to 750°C in the presence of air (reaction times ca. 5 sec). The reactions were found to be intramolecular cyclizations of the type shown in Eq. (1). Conversion rates were 1 to 25% based on the PCB reacted. This formation of PCDFs was judged to be of significant environmental significance in case of accidental burning or incineration of PCBs (13). The experiments resulted

in complex isomeric mixtures of PCDFs. The reactions apparently led easily and exclusively to PCDFs; neither PCDDs nor PCBP were observed.

In further model experiments using individual, specially synthesized PCB isomers, we identified three main and a fourth, minor reaction route leading to PCDFs [Eq. (2)] (18). These reactions involved the loss of *ortho*-Cl₂, the loss of *ortho*-HCl with and without 2,3-chlorine shift, and finally the loss of *ortho*-H₂. The last reaction was only of some importance for a few specific PCB isomers; the formation of PCDFs from PCBs was found to proceed mainly via reaction pathways 1-3. The PCDFs formed predominantly contained thus one or two chlorines fewer than the PCB precursors. Eighteen different PCB isomers were investigated and more than 40 PCDFs were observed. These reactions leading to very specific PCDF isomers were also used for the preparation of small quantities of PCDF reference compounds. More recently all 38 tetra-CDF isomers were prepared via these reaction routes (19).

Conversion rates were in the per cent range at optimal temperatures of 500-600°C. At 700°C, the degradation rates were faster than the rates of formation; at temperatures above 800°C, PCBZs were the only identifiable products beside CO₂, HCl and carbon.

The same reactions were also found to occur with the bromo analogs. Firemaster BP-6, a flame retardant with 2,4,5,2',4',5'-hexabromobiphenyl as a main component, was converted into toxic 2,3,7,8-tetra-bromodibenzofuran (13,20). The thermal conversion of polybrominated biphenyls (PBBs), and of polychlorinated and polybrominated diphenyl ethers (PCDPEs), used as flame retardants and in electrical appliances (TV covers), into toxic products (21) raises serious concern, and the use of these products in these applications should be carefully reconsidered.

From the four reaction pathways it is possible to deduce the structure of the PCDF isomers expected from the thermolysis of the various PCB isomers present in commercial formulations. Two commercial PCBs (Aroclor 1254 and 1260) were analyzed for individual PCB isomers by using high-resolution gas chromatography (HRGC) and mass spectrometry in comparison to authentic reference compounds. In Table 3 we list the major PCB components found in these formulations and the PCDFs expected by the four reaction pathways. Aroclor 1254, consisting primarily of tetra-, penta-, hexa- and heptachlorobiphenyls and small amounts of tri- and octachlorobiphenyls, is expected to yield di-, tri-, tetra-, penta- and hexa-CDFs; Aroclor 1260 consisting primarily of penta-, hexa-, hepta- and octachlorobiphenyls is expected to yield tri-, tetra-, penta-, hexa- and hepta-CDFs. It is seen from Table 3 that the PCDFs expected include the toxic 2,3,7,8-substituted isomers.

Analysis of the thermolysis products of Aroclor 1254 and 1260 in fact confirmed these predictions. From these pyrolyses, about 30 major and more than 30 minor PCDF isomers were observed, with total yields in the range

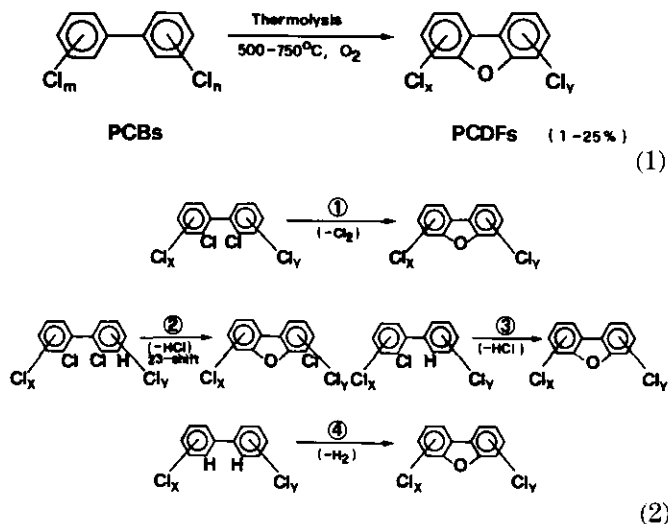


Table 3. Main PCB components in commercial PCB formulations (Aroclor 1254 and 1260) and PCDF isomers expected from their thermolysis.

PCB isomers found ^a		PCDF isomers expected by various reaction routes ^b			
In Aroclor 1254	In Aroclor 1260	Route (1)	Route (2)	Route (3)	Route (4)
2,5,2',5'		2,8	2,4,8	1,4,8	1,4,6,9
2,3,2',5'		2,6	2,4,6	1,4,6; 1,2,8	1,2,6,9
2,5,3',4'		—	—	2,6,7; 2,3,8	1,4,7,8
2,3,6,2',5'	2,3,6,2',5'	1,4,8; 1,2,8	1,4,6,8; 1,2,6,8; 1,2,4,8	1,2,6,9; 1,4,6,9	—
2,4,5,2',5'	2,4,5,2',5'	2,3,8	2,3,6,8; 2,3,4,8	1,4,7,8; 1,3,4,8	1,3,4,6,9
2,3,4,2',5'		2,6,7	2,4,6,7	1,2,3,8; 1,4,6,7	1,2,3,6,9
2,3,6,3',4'		—	—	1,4,7,8; 1,4,6,7; 1,2,7,8; 1,2,6,7	—
2,4,5,3',4'		—	—	2,3,7,8; 2,3,6,7	1,3,4,6,7; 1,3,4,7,8
2,3,4,3',4'		—	—	2,3,6,7; 3,4,6,7	1,2,3,6,7; 1,2,3,7,8
2,3,6,2',4',5'	2,3,6,2',4',5'	1,4,7,8; 1,2,7,8	2,3,4,6,9; 2,3,4,8,9; 1,2,4,7,8	1,3,4,8,9; 1,3,4,6,9	—
2,4,5,2',4',5'	2,4,5,2',4',5'	2,3,7,8	2,3,4,7,8	1,3,4,7,8	1,3,4,6,7,9
2,3,4,2',3',6'		1,4,6,7; 1,2,6,7	1,2,4,6,7	1,2,3,8,9; 1,2,3,6,9	—
2,3,4,2',4',5'	2,3,4,2',4',5'	2,3,6,7	2,3,4,6,7	1,3,4,6,7; 1,2,3,7,8	1,2,3,6,7,9
2,3,4,2',3',4'		3,4,6,7	—	1,2,3,6,7	1,2,3,7,8,9
	2,3,5,6,2',4',5'	1,2,4,7,8	1,2,4,6,7,8	1,2,4,6,7,9	—
	2,3,4,5,2',3',6'	2,3,4,6,9; 2,3,4,8,9	1,2,3,6,7,8	1,2,3,4,6,9; 1,2,3,4,8,9	—
	2,3,4,5,2',4',5'	2,3,4,7,8	2,3,4,6,7,8	1,3,4,6,7,8; 1,2,3,4,7,8	1,2,3,4,6,7,9
	2,3,4,5,2',3',4'	2,3,4,6,7	—	1,2,3,4,6,7; 1,2,3,6,7,8	1,2,3,4,7,8,9
	2,3,4,5,2',3',5',6'	1,2,4,6,7,8	—	1,2,3,4,6,8,9	—
	2,3,4,5,2',3',4',5'	2,3,4,6,7,8	—	1,2,3,4,6,7,8	1,2,3,4,6,7,8,9

^aAnalysis by HRGC and mass spectrometry, major components in italics, subscripts tetra- to octa- omitted.

^bSubscripts di-, tri- etc. omitted; 2,3,7,8-substituted tetra-, penta- and hexa-CDF isomers in italics.

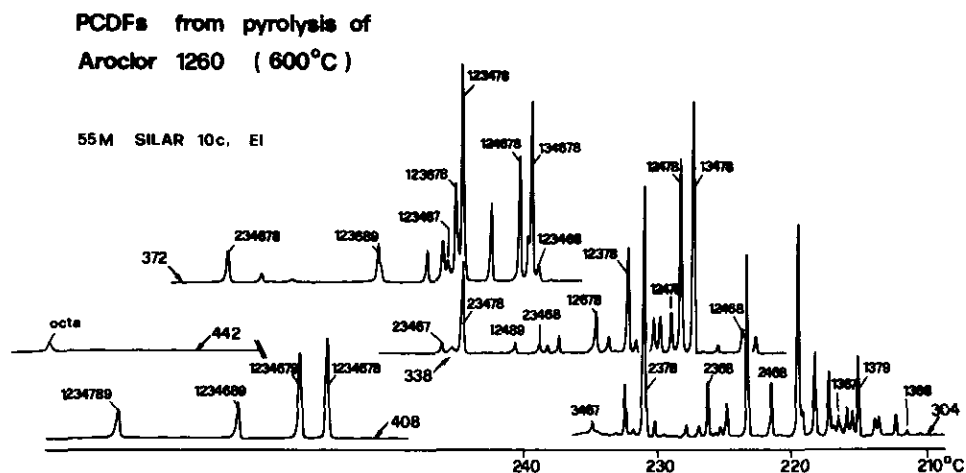
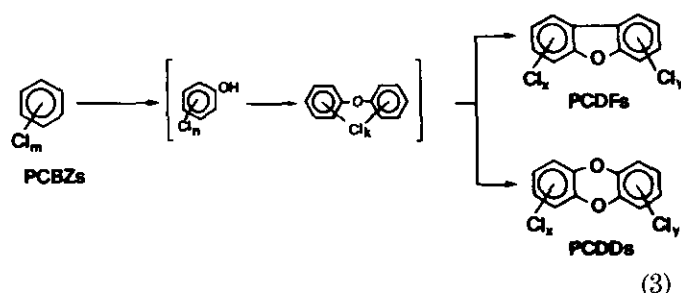


FIGURE 2. Chromatogram (SID mass spectral analysis, EI, m/z 304, 338, 372, 408 and 442) showing elution of tetra-, penta-, hexa-, hepta- and octa-CDFs in pyrolyzed Aroclor 1260. Among identified isomers were 2,3,7,8-substituted congeners.

of 3–25% of the PCB reacted. A chromatogram of pyrolyzed Aroclor 1260 is shown in Figure 2. Among the PCDF isomers observed from Aroclor 1254 were 2,3,7,8-tetra-, 1,2,3,7,8- and 2,3,4,7,8-penta-CDF; in case of Aroclor 1260, additionally 1,2,3,4,7,8-, 1,2,3,6,7,8- and 2,3,4,6,7,8-hexa-CDF were observed; 2,3,7,8-tetra-CDF was the predominant isomer. Obviously, the hazardous 2,3,7,8-substituted PCDFs expected are those actually formed as main components in the thermolysis of these commercial PCB formulations.

Formation of PCDFs and PCDDs from the Thermolysis of PCBs

In subsequent experiments, we observed the formation of tricyclic aromatic compounds in thermolytic reactions from PCBs (14). The main products were PCDFs in yields of up to 1%, and PCDDs in somewhat smaller yields. Because chlorophenols were also observed, the reactions presumably start with oxidation of PCBs followed by condensation to PCDFs and



PCDDs, possibly by way of PCDPEs as shown in the tentative reaction scheme in Eq. (3). These condensations are bimolecular and require the presence of higher concentrations of PCBZs to proceed efficiently. PCBZs can be formed from other chlorinated organic compounds including PVC (22) and possibly even from inorganic chloride and organic materials under pyrolytic conditions; however, the amounts of PCBZs and the concentrations reached by these routes are probably too low to represent an intolerable risk for the formation of PCDFs and PCDDs. The situation, however, may be different, if attempts were made to dispose of larger quantities of PCBZs such as wastes and residues from industrial chemical processes by incineration. Strict controls have to be implemented for such processes in order to ensure safe disposal and to prevent environmental contaminations and occupational exposures to PCDFs and PCDDs (14).

The actual reaction mechanisms have not been elucidated in these experiments. They seem rather complex involving multiple rearrangements, as indicated from the pyrolysis of 1,2,4-trichlorobenzene that gave a complex mixture of PCDFs (at least 10 tetra-, 18 penta-, 14 hexa-, and all 4 hepta-CDFs were observed) as well as tetra-, penta- and hexa-CDDs. Pyrolysis of 1,2,4,5-tetrachlorobenzene similarly gave a complex mixture of penta-, hexa-, hepta- and octa-CDF, and smaller amounts of hexa-, hepta- and octa-CDD, again indicating extensive rearrangements. No PCBPs were observed in these experiments.

Search for Other Chlorinated Tricyclic Aromatic Compounds from Reactions Involving PCBs and PCBZs

The previous experiments clearly showed that PCBs produced primarily PCDFs in thermolytic reactions, whereas PCBZs formed both PCDFs and PCDDs. In these experiments no other tricyclic aromatic compounds such as PCBPs or other chlorinated polynuclear aromatics (PCPNAs) were observed. However, in samples from several sites of accidents with electrical systems containing PCBs and PCBZs such compounds were detected (1,2). A number of PCBPs and PCPNAs (parent molecular weight 202 daltons), tentatively identified

as polychlorinated pyrenes/fluoranthenes (PCPYs), were observed. PCBPs conceivably could be formed from PCBs via an intramolecular cyclization (abstraction of Cl_2 or HCl) or from condensation of PCBZs, possibly via benzyne.

In the previous thermolysis experiments, the formation of PCDFs and PCDDs required the presence of oxygen (air). In a series of additional experiments, we investigated thermolytic reactions (vacuum pyrolyses, 600 and 750°C) under exclusion of oxygen for the possible formation of PCBPs from commercial PCBs (Aroclor 1254), individual PCB isomers (2,3,6,2',5'-penta- and 2,4,5,2',4',5'-hexachlorobiphenyl) and PCBZs (1,2,4-tri- and 1,2,4,5-tetrachlorobenzene). However, again no indication was obtained on any significant formation of PCBPs. The major reaction pathways observed were dechlorination of PCBs and formation of PCBZs, HCl and carbonization. Trace amounts of PCDFs and two PCBP isomers were observed. Apparently, the formation of PCBPs is not a major route in these thermolytic reactions. Additional preliminary laboratory experiments investigating electrical discharge conditions (arcing by a 30 kV sparktester) on Aroclor 1254 gave no detectable quantities of PCDFs or PCBPs.

Analysis of Polychlorinated Tricyclic Aromatic Compounds

The analysis of polychlorinated tricyclic aromatic compounds is complicated by the extremely low detection levels required (due to the high toxicity of some of the compounds), the many additional, co-extracted, very often chlorinated compounds present, and the large numbers of isomers involved. Very sensitive, selective and specific analytical techniques are required. There have been great efforts undertaken and a wealth of information is available on analytical methods; several international conferences and workshops were devoted to PCDDs and PCDFs. The most specific methods described use mass spectrometry for detection, quantification and confirmation of these compounds. A more detailed description of the analysis of these compounds in environmental samples is given elsewhere (23). In that article, we emphasize the importance of isomer identifications and of isomer-specific analyses, especially of 2,3,7,8-substituted isomers. Extraction and cleanup procedures are required that recover most or all of the PCDFs, PCDDs and possibly PCBPs as a group. HRGC analysis is used for the separation of isomers; electron-impact (EI) and negative chemical ionization (NCI) mass spectrometry are used for detection and identification. Combined mass spectrometry-mass spectrometry (MS-MS) is potentially useful but has not yet been investigated here. The identification of PCDFs and PCDDs is usually easily accomplished by mass spectrometry, but that of PCBPs is more complicated because of interference from PCBs (23).

All PCDFs and PCDDs containing four or more chlor-

indicated, the major PCDFs observed in this soot sample were those produced from these pyrolyses, suggesting PCBs as primary precursors of the PCDFs, although some contribution of PCDFs from PCBZs may also be present.

In Figure 4 we show a chromatogram of the PCDD analysis of the same Binghamton soot sample. The results are quantified in Table 5. As indicated, the combined level of PCDDs is around 20 ppm, about 100 times

Table 4. PCDF isomers found in soot from transformer accident in Binghamton, NY and in PCB pyrolyzates.

PCDF isomer	Level of PCDFs observed in soot, ppm ^a	Isomers in PCB pyrolyzates ^b
2,3,7,8-Tetra-CDF	12	***
1,3,7,9-Tetra-CDF	1	*
Others	15 (4)	
1,2,3,7,8-Penta-CDF	310	***
2,3,4,7,8-Penta-CDF	48	***
1,2,4,7,8-Penta-CDF	25	***
1,2,4,7,9-Penta-CDF	22	*
1,3,4,7,8-Penta-CDF	65	***
2,3,4,8,9-Penta-CDF	25	*
1,2,3,6,7-Penta-CDF	60	*
2,3,4,6,7-Penta-CDF	12	*
Others	110 (12)	
1,2,3,4,7,8-Hexa-CDF	310	***
1,2,3,6,7,8-Hexa-CDF	150	***
2,3,4,6,7,8-Hexa-CDF	10	*
1,2,3,4,6,8-Hexa-CDF	30	*
1,2,3,6,8,9-Hexa-CDF	38	*
1,2,4,6,7,8-Hexa-CDF	50	***
1,3,4,6,7,8-Hexa-CDF	125	***
Others	250 (8)	
1,2,3,4,6,7,8-Hepta-CDF	230	***
1,2,3,4,6,7,9-Hepta-CDF	120	***
1,2,3,4,6,8,9-Hepta-CDF	55	*
1,2,3,4,7,8,9-Hepta-CDF	55	*
Octa-CDF	40	*

^aApproximate number of additional isomers given in parentheses.

^bLaboratory experiments using Aroclor 1254 and 1260; major isomers found denoted by ***, others by *.

lower than the level of PCDFs, indicating the contamination to be primarily due to the latter compounds. Maximum level was found for the hepta-CDDs, somewhat smaller levels of tetra-, penta-, hexa- and octa-CDD were observed. Again, 2,3,7,8-substituted isomers were present, including 2,3,7,8-tetra-, 1,2,3,7,8-penta- and to a lesser degree all three toxic hexa-CDDs. The sources of these PCDDs are very likely PCBZs present in the transformer fluid (23% tri- and 12% tetrachlorobenzene); we previously reported the formation of tetra- to octa-CDDs from tri- and tetrachlorobenzenes in our thermolysis experiments (14). In addition to PCDFs and PCDDs, the presence of some PCBP was reported (2); however, isomers were not identified.

In addition, we investigated a soot sample (courtesy S. Räisänen) from a capacitor accident in a powerstation of an industrial site in Finland. Previous analyses by Finnish authorities had shown levels of PCDFs of up to 20 µg/m² in the contaminated area. In Figure 5, we show a chromatogram of a benzene extract of a soot sample

Table 5. PCDD isomers found in soot from transformer accident in Binghamton, NY.

PCDD isomer	Level of PCDDs observed in soot, ppm ^a
2,3,7,8-Tetra-CDD	0.6
Others	0.6 (4)
1,2,3,7,8-Penta-CDD	2.5
Others	2.5 (7)
1,2,3,4,7,8-Hexa-CDD	0.7
1,2,3,6,7,8-Hexa-CDD	0.6
1,2,3,7,8,9-Hexa-CDD	0.4
1,2,3,4,6,8/1,2,4,6,7,9/1,2,4,6,8,9-Hexa-CDD	1.2
1,2,3,6,8,9/1,2,3,6,7,9-Hexa-CDD	1.3
1,2,3,4,6,7-Hexa-CDD	0.5
1,2,3,4,6,7,9-Hepta-CDD	4
1,2,3,4,6,7,8-Hepta-CDD	3
Octa-CDD	2

^aNumber of other isomers given in parentheses.

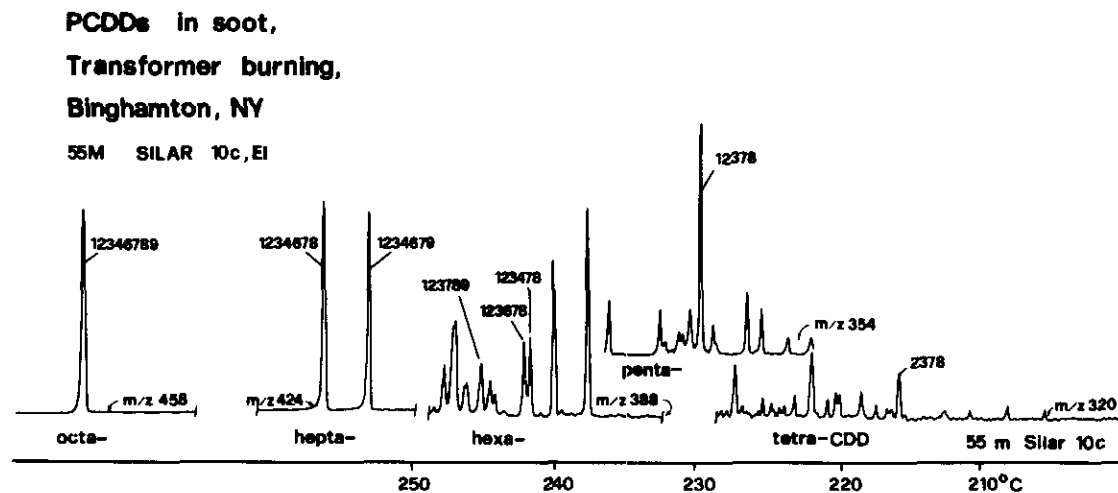


FIGURE 4. Chromatogram (SID mass spectral analysis, EI, m/z 320, 354, 388, 424 and 458) showing elution of tetra-, penta-, hexa-, hepta- and octa-CDDs in soot sample (see Fig. 3).

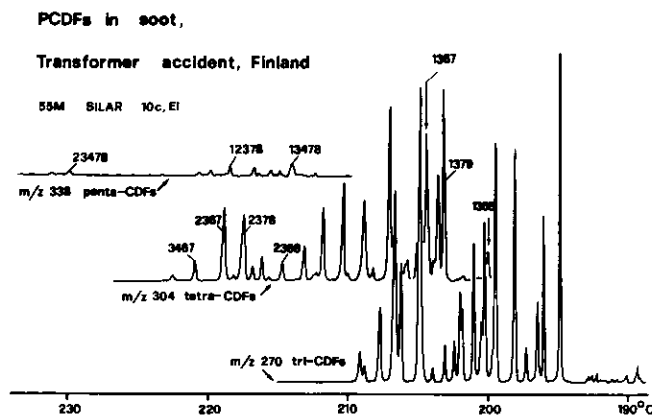


FIGURE 5. Chromatogram (SID mass spectral analysis, EI, m/z 270, 304 and 338) showing elution of tri-, tetra- and traces of penta-CDFs in an extract of soot recovered after a capacitor accident in power station at an industrial complex in Finland.

Table 6. PCDF isomers found in soot from capacitor accident in Finland (1982).

PCDF isomer	Level of PCDFs observed in soot, ppm ^a
Tri-CDFs	270 (19)
2,3,7,8-Tetra-CDF	3
1,3,6,8-Tetra-CDF	1
1,3,7,9-Tetra-CDF	10
1,3,6,7-Tetra-CDF	7
2,3,6,8-Tetra-CDF	2
2,3,6,7-Tetra-CDF	4
3,4,6,7-Tetra-CDF	1
Others	24 (13)
1,2,3,7,8-Penta-CDF	1-2
2,3,4,7,8-Penta-CDF	
1,2,4,7,8-Penta-CDF	
1,3,4,7,8-Penta-CDF	
1,2,4,7,9-Penta-CDF	
1,2,3,6,7-Penta-CDF	
1,2,6,7,8-Penta-CDF	
2,3,4,6,7-Penta-CDF	

^aNumber of other isomers given in parentheses.

analyzed for PCDFs (55 m Silar 10c HRGC column, EI mass spectrometry); quantitative results are reported in Table 6. Again a rather complex isomeric mixture of PCDFs is observed, consisting primarily of tri- and tetra-CDFs with small amounts of penta-CDFs, including to a smaller degree some 2,3,7,8-substituted isomers. The combined level of tetra- and higher chlorinated PCDFs is 54 ppm, significantly lower than in the Binghamton sample. The major PCDFs in the Finnish sample are lower chlorinated than in that previous sample, indicating involvement of a lower chlorinated PCB. No PCDDs (smaller than 1% relative to the PCDFs) and only very minor amounts of some PCBPs and other PCPNAs were observed. Apparently no PCBZs were involved in this accident.

Analyses of samples from accidents involving malfunctioning electrical systems have demonstrated that conversion of PCBs and PCBZs into toxic derivatives (PCDFs, PCDDs and PCBPs) is possible. Model ex-

periments have unveiled reaction routes to some but not all of these tricyclic aromatic compounds. Further investigations should establish additional routes and the exact conditions required for these formations. Such knowledge is indispensable for taking suitable measures to prevent such accidents and environmental contaminations with these hazardous compounds.

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